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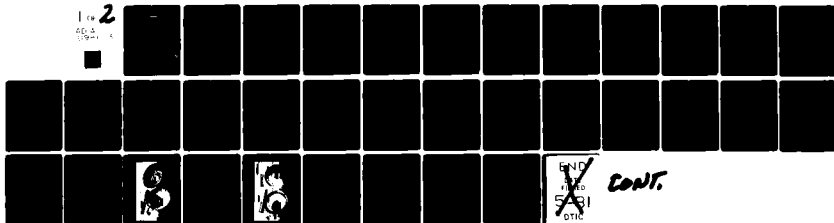
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AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

FUELS COMBUSTION RESEARCH

For the Period 1 October 1979 to 30 September 1980

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Prepared by:

Irvin Glassman

Irvin Glassman
Professor
Co-Principal Investigator
Correspondent

Frederick L. Bryer

Frederick L. Bryer
Associate Professor
Co-Principal Investigator

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School of Engineering and Applied Science
Department of Mechanical and Aerospace Engineering
PRINCETON UNIVERSITY
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ABSTRACT (Continue on reverse side if necessary and identify by block number) A high temperature sampling system for the Princeton flow reactor has been developed. Initial results have been obtained on the oxidation of toluene. Benzaldehyde forms as an important intermediate and then the process becomes one of the oxidizing formyl and phenyl reactions. The effects of oxygen index and temperature on sooting diffusion flames have been studied. Results indicate that the stoichiometric flame temperature dominates the sooting tendency and that the C4 and C5 olefine and diolefins and the aromatics are the most dominant sooting fuels. In development, as well as a powerful fuel.		

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→ sensitivity analysis tools to quantitatively address the complex interaction between a combustion system's chemical and transport component.

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ABSTRACT

Recognizing the uncertainties as to future available fuel sources and characteristics, A.F.O.S.R. established a Center of Excellence in Combustion Related Fuel Problems. The program concentrates on chemical aspects of combustion problems. This document is the Annual Report for the period 1 October 1979 to 30 September 1980 and reports solely on the research progress made.

Results on a detailed and overall reaction mechanism for propane pyrolysis have been published. Some of the first results on the high temperature oxidation of aromatics have been obtained. Most of this work has been with toluene and a general mechanism of toluene oxidation has been proposed. The important intermediate formed is benzaldehyde and the process evolves into the oxidation of formyl and phenyl radical. The indications are that all the alkylated aromatics follow the sequence of initial oxidation of the alkyl group and then the oxidation of phenyl radical. If so, complexities with respect to overall kinetic modelling for aromatics may not exist. The excellent data obtained are due in great part to the development of a high temperature sampling system for the Princeton flow reactor and this system is a significant contribution in itself.

Extensive results are reported on the sooting tendencies of fuels. In particular the effects of oxygen index and temperature on sooting diffusion flames have been evaluated. Results verify our earlier postulate that it is the stoichiometric flame temperature and the fuel structure that determine sooting tendencies in diffusion flames. The temperature based on the overall stoichiometry based the flow rates of fuel and oxidizer is not important. The oxygen concentration in the far field as it affects burn-up rate is important.

Combustion phenomena inherently involves a complex interaction of many simultaneous reactions and associated transport phenomena. Efforts to develop a

powerful family of sensitivity analysis tools to quantitatively address the complex interaction between a combustion system's chemical and transport components are detailed.

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I. INTRODUCTION

The importance of chemically-related combustion problems has led to the establishment of an integrated fuels research program under A.F.O.S.R. support. This document is the annual report of progress under that effort for the contract year 1 October 1979 to 30 September 1980.

Research emphasis is entered on the pyrolysis and fuel-rich oxidation of the aliphatic and aromatic hydrocarbons, the controlling mechanisms of soot formation and destruction, and sensitivity analysis techniques as applied to combustion problems. The progress made and results obtained during the subject contract year are reported in the following sections.

II. HYDROCARBON OXIDATION AND PYROLYSIS

Work on the pyrolysis of propane was completed before the contract period began, however the writing and publication of the material proceeded into the period of concern. The paper entitled "An Overall and Detailed Kinetic Study of the Pyrolysis of Propane" by D.J. Hautman, R.J. Santoro, F.L. Dryer and I. Glassman was accepted for publication in the International Journal of Chemical Kinetics¹.

After the completion of this work, our efforts concentrated on the very important problem of the oxidation of aromatics. OSHA regulations at the time the study began forbade the use of benzene, consequently our initial efforts concentrated on toluene.

As all previous oxidation studies, the work was performed on the Princeton turbulent flow reactor. The use of the aromatics in the reactor posed substantial problems in sampling and analysis of species formed during the oxidation process. Whereas, in the oxidation of aliphatics, experience had shown that the species formed were low boiling point compounds whose peaks in gas chromatographic analysis were readily known; it was to be expected in the aromatic work that much

heavier species would be found.

The presence of unknown high boiling point species necessitated the development of a unique sample storage technique. The development of this technique and the successful functioning and use of our GC/MS apparatus were major accomplishments during the subject year, but more importantly, permitted us to obtain sufficient data on the oxidation of toluene to begin to understand its complex mechanism.

A. New Sampling System

Both temperature and species profiles are measured along the length of the reactor duct. The temperature is measured, as in earlier flow reactor studies, with a silica coated Pt 30% Rh/Pt 6% Rh alloy thermocouple with a bead diameter of .0015" and a spatial resolution of about twenty bead diameters. Dryer² has discussed this technique at length in an early Ph.D. thesis under A.F.O.S.R. sponsorship.

The gas sampling techniques, in principle, are also those used in earlier flow reactor studies: combustion gases are withdrawn from the reactor with a water cooled probe and are stored for later analysis by a gas chromatograph. A major purpose of the present work, however, was to develop a sample acquisition and storage system which operates at temperatures above ambient to prevent condensation and polymerization reactions. This system, which replaces the ambient temperature glass bottle storage system previously in use, consists primarily of

1. a variable temperature probe coolant system for quenching of the combustion gases at a controlled temperature
2. a heated multiposition sample storage valve with sixteen 12 cc. storage loops
3. heated gas transfer equipment which comprises the interface between the multiposition valve and either the flow reactor or a gas chromatograph

The final design of the heated sampling system was the result of essentially two stages of development. The first stage focussed on the problems associated with high temperature acquisition and storage of samples and resulted in the choice of a multiposition valve as the principal storage device. As development of this first generation system proceeded, however, several problems were identified, all of them associated with operational characteristics of the valve. The second generation system, through a more indirect approach to the storage problem, circumvented the valve limitations and retained the essential features of the first design. The fundamental problems of high temperature storage and the operation-related valve problems were all minimized or eliminated in the second system. Both systems are discussed below because an understanding of the system's evolution will provide insights into the details of its final design and into the limitations of its use.

Successful chemical sampling involves satisfactory accomplishment of each of the following goals:

1. isolation of a flow of reactive media from a specific point in the reaction environment
2. prevention of further chemical or thermodynamic alteration of the contained species
3. introduction of a defined quantity of this sample, intact, to an analytical instrument

The room temperature system previously used in our A.F.O.S.R. kinetic studies reasonably satisfied these requirements (for known stable species except formaldehyde). It incorporated storage of samples in glass bottles at room temperature and required pressurization of the samples (for injection onto a gas chromatograph) by displacement of a sample volume with mercury.

Condensation, which was not a problem in earlier flow reactor studies (because the fuels considered in those studies gave rise to intermediate species and products which were gases or high vapor pressure liquids at room temperature), was confirmed early as a problem in the aromatics studies. First, a yellow-brown gummy film was noted on the outer surface of the sampling probe following aromatic oxidation runs. Second, a carbon balance through the reaction for aromatic oxidation data gathered with the older sampling system showed a loss in total carbon content in the intermediate stages of the reaction, where high boiling point intermediates are likeliest to exist. And third, an examination of the available literature revealed postulated and observed intermediates of critical importance which have extremely small vapor pressures at the quench temperatures used with the older sampling system. Though it is impossible, *a priori*, to theoretically estimate the magnitude of a condensation problem -- the intermediates and their concentrations would need to be known for such a calculation -- the heated sampling and storage approach suggested here seemed reasonable for two reasons. First, it allows for positive determination of whether or not a condensation problem exists; and second, it is designed for easy upgrading to higher temperatures if a problem is identified and persists with the present system.

The system described here, at the very least, allows for definitive analysis of the condensation problem. This was not possible with the room temperature system because the condensation limited partial pressures at ambient temperatures of some possible critical intermediates (e.g. hydroquinone and pyrocatechol) are below the detection limits of the flame ionization detector (FID) used for the analysis. In other words, at room temperature, insufficient amounts of these intermediates remain in the gas phase for detection (for sample sizes appropriate to gas chromatographic analysis of other species). At the higher quench temperatures of the heated system, this is not the case, and these high boiling point

species can be identified and quantified. Comparison of the amount detected with the vapor pressure of the species at the sampling temperature will, in turn, allow determination of the species, if any, which are condensing. The system can then be upgraded to a point where the tradeoff between the condensation of stored gases and their reactivity is optimized.

There are two advantages to controlling condensation in this way. First, major high boiling point intermediate species can be accurately measured. But additionally, minor aromatic species -- which will not greatly affect the carbon balance or an "overall" analysis of the data -- can be detected, identified, and quantified. The heated sampling system interfaces with our GC/MS in a manner completely analagous to its GC interface, and allows ready identification of species which are impractical to identify with a GC alone and which would be lost to condensation at room temperature.

The storage temperature of 70°C has a second advantage related to the integrity of the stored sample: by preventing polymerization reactions associated with the storage of formaldehyde at room temperature, it should allow accurate formaldehyde analysis.

Also, the heated sampling system has the advantages of preventing exposure of stored samples to light and to adsorptive surfaces (e.g. mercury, systhetic rubber), both of which occurred in the older system. All surfaces which contact sample gases in the heated sampling system are stainless steel, so the exposure to light that resulted from storage in glass bottles on an exposed sampling rack is circumvented. Furthermore, gases are pressurized for injection with a stainless steel welded bellows pump and not with the mercury system previously in use.

The heating of a number of stored samples warrants a more compact system than the glass bottles previously in use. Further, the transfer and handling of individual hot samples for analytical purposed requires either the use of a sep-

arate heated and insulated oven for each sample or a method of remote control of a collection of samples in a single heated environment. A remotely actuated multiposition valve with several storage loops satisfies both of these requirements (Figure 1).

The most direct approach to the use of such a valve as the storage unit for a gas sampling requires a system which consists primarily of three components: the probe coolant system, the gas transfer equipment (including the lines, the pump and the manostat), and the sample storage system (the multiposition valve). Wherever necessary, the components are heated to prevent condensation.

Our sampling probes are constructed of 304 stainless steel and are cooled by two water jackets, one inside the other. The temperature of the water passing through the jackets at the probe inlet can be varied between about 15°C and 80°C. Through control of this water temperature, the temperature to which the combustion gases are quenched can be controlled.

The probe coolant system consists simply of a recirculating water stream which is successively cooled by a heat exchanger and heated by the hot reactor (through the probe). Since heat addition to the coolant stream varies as the probe is extended into the reactor, variable heat transfer at the heat exchanger is required to produce the isothermal quench temperature chosen for a study. This is accomplished with a remotely actuated valve that varies the secondary flow rate through the heat exchanger.

Operation of the first generation sampling system was as follows: combustion gases were withdrawn from the reactor through the probe and a length of heated line by a heated stainless steel welded bellows pump. The bellows pump raised the pressure of the sampled gases above atmospheric pressure, and the flow proceeded through a heated 7 micron filter and a temperature equilibration coil to the sample storage valve. The temperature equilibration coil and the sixteen loop

storage valve were contained in a separate, portable, thermostatted oven assembly. The pressure of the gases being sampled was controlled by a manostat/vacuum pump system downstream of the valve. Each of the valve loops had a pre-determined volume of .5 cc. When the valve was actuated and the flow switched from one loop to the next, a defined quantity of sample was trapped in the first loop (P, V and T are all defined). Up to fifteen samples could be stored in this way, with the remaining loop open to the flow path. Once filled, the multiposition valve system was carried (in its oven) to a gas chromatograph, where the loops were flushed, one by one, into the GC columns for analysis. In this design, the pressure, volume and temperature of the stored sample were chosen to accommodate gas chromatographic sample size requirements.

This system fulfilled in principle each of the sampling system requirements outlined: defined quantities of sample were isolated and trapped in the multiposition valve loops; the storage temperature was low enough to prevent significant reaction, but high enough to prevent condensation or polymerization; and the samples were transferred directly to a gas chromatograph for analysis. Nowhere in the transfer or storage of samples were they exposed to light or made to contact adsorptive substances like mercury or synthetic rubber. (The adsorptive sites on the stainless steel in the system were most likely pacified during the flushing of sample through the system during sample acquisition). Unfortunately, operational limits of the multiposition valve give rise to several problems outlined below:

1. Loop to Loop Volume Variations - The volumes of the sixteen loops were difficult to match, so sample sizes vary slightly. Calibrating each loop individually could have eliminated this problem, but at the cost of additional analytical work.

2. Leakage into or out of the Loops or Valve Body - No leaks through individual loops were identified, but a small, progressive loss of sample over time was observed when samples were stored at above atmospheric pressure. Leakage out made determination of exact sample size impossible. The inverse problem of leakage in for storage at sub-atmospheric pressure lead to dilution and distortion of particular species (especially oxygen).
3. Destruction of Stored Samples due to Passage of High Pressure GC Carrier Gas Through the Multiposition Valve - This was a large effect. Since the GC carrier gas must enter the chromatographic columns at about 60 psig in order to overcome the resistance of the columns, helium at 60 psig must pass through the multiposition valve in order to flush the samples onto the columns. Although the manufacturer specifies that the valve sealing is good to 400 psig, we found that flushing the samples with high pressure helium caused significant distortion of four out of fifteen stored samples. The four that were destroyed were always the first and last three loops analyzed, no matter which loop was chosen as the starting point. Different loops were chosen as the starting point. The pattern and magnitude of the distortion was clear, though the mechanism was uncertain.
4. Diffusion of Sample Between Adjacent Loops - The manufacturer of the multiposition valve specified a diffusion rate of 1.0×10^{-6} torr-liters/sec. of helium, a value roughly substantiated by tests conducted in this laboratory. For the sample sizes chosen for accurate chromatographic analysis (about .5 cc. - atm.), and for storage times (25+ hours) required for analysis of fifteen samples containing the species expected in aromatics oxidation reactions, this small rate could significantly alter stored samples. The diffusion distortion was demonstrated by filling the sample valve loops with either calibration gas (CH_4 , C_2H_4 , C_2H_6 , C_3H_8 , CO , CO_2 in N_2) or pure N_2 and analyzing

the stored samples over time. Errors in excess of 15% were measured in less than 25 hours.

These four problems, especially the last three, made this critical approach to storage and analysis of samples unacceptable. The design philosophy had to be changed, and in the second generation system, the errors resulting from the problems discussed above were either eliminated altogether or made negligibly small.

Figure 2 shows a schematic of the new system. Again, samples are drawn through the probe with a heated bellows pump and stored in loops on a sixteen-position valve. But the volume of each of the loops has been increased from .5 cc. to 12 cc. (Figure 3), and the storage pressure is now about 2 atmospheres instead of .5 atmospheres. The higher pressure is achieved by simply replacing the manostat/vacuum system of the previous design with a needle valve, which throttles the flow to achieve the desired value. Although throttling causes a drop in the flow rate through the system, less than two sweep volumes are required to ensure complete displacement of any residual gases in the transfer lines, and the system is designed to achieve this easily. Both flow rate and pressure are measured at the outlet of the multiposition valve.

The new system stores almost 50 times the sample size appropriate for GC analysis. A less direct approach to injection of samples onto the chromatographic columns was therefore necessary. A secondary 1 cc. sample loop is now used to set the sample size for analysis. This sample loop is connected on the inlet side to the multiposition valve (i.e. to the stored samples) through a length of heated line, and on the outlet side to a manostat/vacuum system. When the multiposition valve is actuated and a new storage loop is exposed to the sample line, the gases in the 12 cc. loop, which are stored at 2 atmospheres, flow through the 1 cc. secondary sample loop until the pressure in the whole system is equilibrated to .5 atmospheres by the manostat. Sufficient excess sample is stored in the mul-

tiposition valve loops to assure complete displacement of any residual gases in the secondary sample valve and transfer lines. The .5 cc.-atm. sample in the secondary sample valve is then injected onto the gas chromatograph columns for analysis. Actuation of both the multiposition valve and the secondary sample valve is controlled by a microprocessor indigenous to the gas chromatograph, so fully automatic analysis of successive samples is possible. This procedure not only assures a constant systematic error, but minimizes sample storage times and reduces dramatically the manpower which must be devoted to the analysis of samples. The previous (manual) injection technique required operator attention throughout the 25+ hour analysis time. Once the present system is interfaced with the gas chromatograph and the GC microprocessor is programmed, no additional operator attention is required for complete analysis.

The importance modification introduced in this second generation design is the separation of the sample storage requirements from the GC sample size requirements. This separation allows a flexibility in parameters that virtually eliminates the problems previously discussed.

Because the sample injected onto the GC columns is set in the same loop each time, the effects of loop volume variability are eliminated. The sample leakage problems are also circumvented: since samples are stored at a positive pressure, gases leak out, not in. Loss of sample at the small rates indicated by earlier tests results in loss of a fraction of the stored sample. This loss is not reflected in the sample set in the secondary sampling valve, since a large excess of sample gas remains in the storage loops under all conditions. Any difficulties associated with passage of high pressure GC carrier gas through the multiposition valve are also eliminated. Finally, the diffusion problem is reduced to a negligible level. Although the absolute diffusion rate remains the same, the much larger quantity of sample stored in each loop dilutes the contamination by a fac-

tor of about fifty.

Several tests were conducted to ascertain the magnitude of the persisting diffusion error. In these tests, as in earlier checks on diffusion errors, loops were alternately filled, at pressures expected during routine operation, with calibration gas and with pure nitrogen. The samples were then analyzed in exactly the way they would be during actual operation. The diffusion of calibration gas into the pure nitrogen loops was then plotted as a function of time. The diffusion rate was calculated to be about 3×10^{-6} torr-liters He/sec., in rough agreement with the manufacturer's specified value, but the distortion of the stored sample is shown to be less than 1%, even for the lightest gas expected in our hydrocarbon oxidation studies (CH_4). Note that since diffusion rates are inversely proportional to the square root of the molecular weight of the diffusing species, errors for most species will be significantly smaller.

In summary, the advantages of the sampling system presented here are:

1. control of the sample acquisition and storage temperatures (up to about 80° C)
2. sample isolation from adsorptive surfaces
3. sample isolation from light sources
4. automation

B. Toluene Oxidation Results

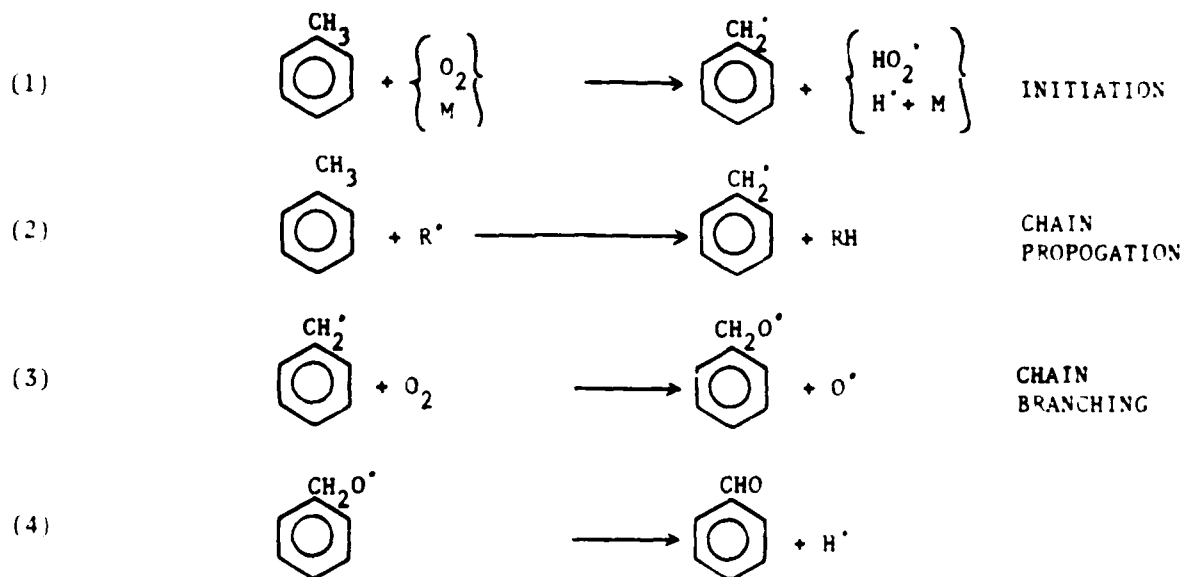
Species profiles typical of those obtained in these early toluene oxidation experiments are given in Figures 4 and 5. All profiles are given in the thesis by Euchner³. Two plots are given for each reaction studied. Note that the mole fraction of carbon is plotted in these figures, not the species mole fraction. Seven times the mole fraction of toluene (C_7H_8) is plotted, for example, while the mole fraction of CO is plotted directly. The equivalence ratio for these experi-

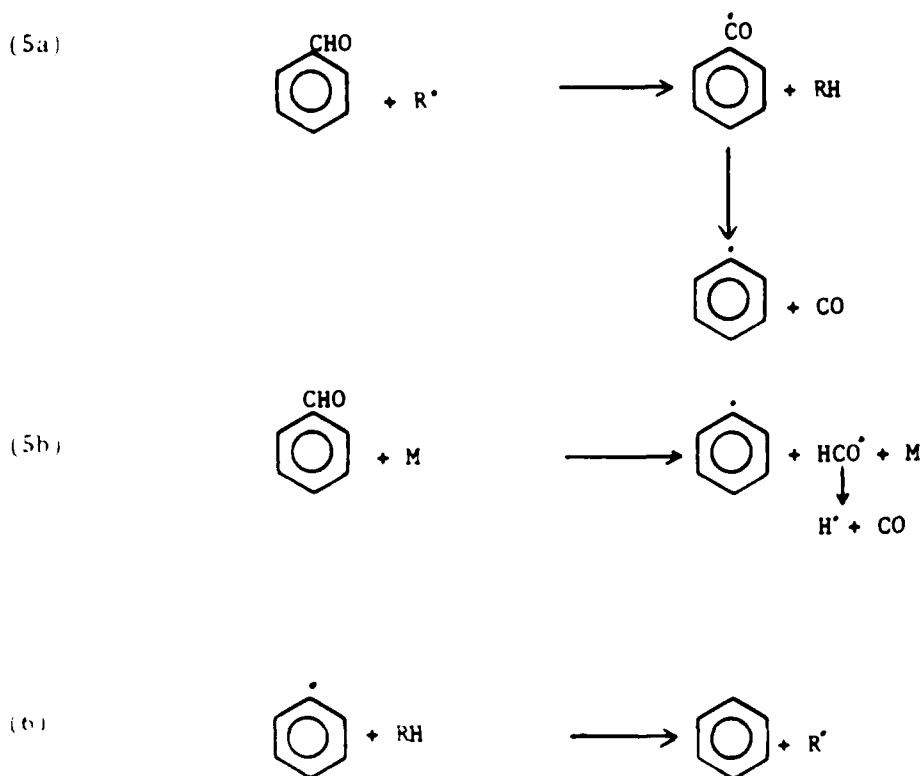
ments was varied between about .06 and .43, and the temperature ranged between 1089 K and 1159 K. The major intermediate species were identified and quantified, though the quantification of minor aromatic species remains uncertain. These GC-MS results confirmed the identifications performed with the GC and gave additional information on species that could not be chromatographically detected. The GC data, which report relative mole fractions of the major intermediates and peak reaction coordinate data for both the major and minor species, give some indication of the mechanism. Note first the general sequential and overlapping trend:



Within the aromatic intermediates, benzaldehyde and benzene are the dominant species, and phenol, styrene (or the xylenes), ethylbenzene and benzyl alcohol are formed in lesser amounts.

The data indicate that, for all conditions studied, the major course of the reaction is through benzaldehyde to benzene, followed by ring fragmentation. The most probable mechanism based on this observation is given below. (R is any radical -- a hydrocarbon radical, H, C, CH or any other radical).






Initiation occurs primarily by abstraction of an alkyl hydrogen from toluene. The strength of a C-H bond in the methyl group is about 85 kcal/mole, significantly less than the strength of the bond between the methyl group and the ring (102 kcal/mole) or the strength of a ring C-H bond (112 kcal/mole).

Most fuel molecules probably then go through some variation of the chain propagating step, Reaction (2), which leads to a large benzyl radical pool.

Chain branching occurs through Reaction (3). Though endothermic, this reaction appears to be the only feasible one at this temperature.

Unimolecular decomposition of the benzyoxy radical to benzaldehyde is postulated in Reaction (4), a step suggested by the large quantities of benzaldehyde and small quantities of benzyl alcohol detected in this study.

The benzaldehyde formed in Reaction (4) could react as in Reactions (5). Radical attack is expected to dominate, especially at lower temperatures. The

aromatic radical thus formed () could decompose easily to form the phenyl radical and CO. Alternately, especially at higher temperatures, benzaldehyde could interact with a second body and decompose into a phenyl radical and a formyl radical. The latter quickly decomposes further into a hydrogen radical and CO, as shown. Similar reactions are well established in the oxidation of aliphatic hydrocarbons. As the temperature was increased in various runs, the amount of benzene relative to benzaldehyde is increased. This trend probably results from an increase in the thermal decomposition of benzaldehyde as the temperature is increased*.

Note that the major products of Reactions (5) are the phenyl radical and CO. The very reactive phenyl radical might easily abstract a hydrogen atom to form benzene, as shown in Reaction (6). Note at this point only that, for six of the seven carbon atoms in a toluene fuel molecule (the ring carbon atoms), the oxidation of toluene appears to reduce to the oxidation of the phenyl radical which should also occur in benzene oxidation (though radical pools are expected to be different in the two cases). Thus the important conclusion of the subject year's work is that the oxidation of toluene the methyl group is oxidation in a manner similar to paraffins and the remaining phenyl radical is then oxidized. Subsequently the possibility exists that the understanding of the oxidation of the alkylated aromatics may hinge only on the mechanism of phenyl oxidation.

III. SOOT FORMATION AND DESTRUCTION

During the previous contract year, we began our initial experimental work on sooting phenomena by dealing with simple diffusion flames and measuring the so-

* Because of the instability of benzaldehyde at these temperatures, further oxidation of benzaldehyde to benzoic acid is expected to be unimportant. It must be noted, however, that benzoic acid would not have been detectable in this study, were it to occur, because it would have been condensed onto the GC columns in the analytical train. The fact that early CO₂ (which would form from the decomposition of benzoic acid) is not evident in the flow reactor profile data, however, lends credence to the supposition that little or no benzoic acid is forming.

called smoke-points or sooting heights. Simultaneous with this effort, Prof. Glassman reviewed the field and published an A.F.O.S.R. report⁴ entitled "Phenomenological Models of Soot Formation in Combustion Systems". Both these efforts provided the direction for the research during the subject contract year. The results obtained have been extensive and of great practical consequence.

Since initial efforts have now been published only the guiding concepts will be detailed here. Essentially the review led us to the conclusions that in pre-mixed flames the dominant factor controlling the tendency to soot was the flame temperature, and that the C/O equivalence ratio in the fuel rich region was only a secondary factor. This conclusion was drawn from the early work of Millikin⁵ who postulated that the sooting tendency in pre-mixed flames was a competition between the rate of formation of the soot precursors and the rate of oxidation attack on these precursors. One could show that as the temperature was raised, the oxidative attack dominated. We further postulated that the trend for aromatics was different due to their oxidative mechanism. Recent results⁶ still indicate this possible, but different from the initially proposed mechanism.

For diffusion flames we postulated that the important factors controlling the tendency of a fuel to soot were the diffusion flame temperature and the fuel structure. However, in the diffusion flames, since there is no oxidative attack on the fuel precursors, the higher the flame temperature, the higher the rate of fuel pyrolysis and precursor formation, and thus the greater tendency to soot.

One of our initial experimental efforts on sooting diffusion flames was to determine the effect of inert additives mixed with the gaseous fuels used. The addition of any inert additive lessened the tendency of the fuel to soot, but, more importantly, we found that the effectiveness of any additive was directly proportional to its molar specific heat. These results tended to support the hypothesis that the temperature was the dominant factor. Consequently we carried

out very extensive controlled series of experiments during the subject contract year.

In order to place the results obtained in the right context, it is worthwhile to review the experimental procedure used. The data were taken on a 1 cm concentric fuel jet surrounded by an air stream flowing in a glass cylinder of about 10 cm in diameter. The volumetric flow rate of the air was sufficiently greater than the fuel flow rate so that the system was always in a highly over-ventilated mode. Diffusion flame heights vary directly with the volumetric flow rate of the fuel. In the concentric configuration used in these experiments, the flame height varies slightly with the surrounding air flow until a certain volumetric rate is reached and then the flame height is independent of the air flow rate. Earlier results by other investigators are inconsistent because they did not recognize this factor.

Every hydrocarbon diffusion flame appears luminous due to the formation of soot. However under low fuel flow rates the amount of soot formed is sufficiently small so that, although the particles become luminous in the high temperature diffusion flame reaction zone, they are burned as soon as the flow streamline carry them into the high temperature oxidizer side of the flame. As the fuel flow rate increases the flame height increases. At a given fuel flow rate sufficient soot apparently forms within the fuel jet so that when the particles flow through the flame they cannot be oxidized and a streak of soot particles appears. In the concentric configuration used an annulus opens up and when the flame is viewed frontally, it looks as if a pair of wings appear. The flame height at which this phenomenon occurs is called the normal smoke point or sooting height and the volumetric or mass flow rate corresponding to this height is used as a qualitative measure of the sooting tendency. Thus the larger the sooting height or volumetric or mass flow rate at this height, the less the tendency to soot; and vice-versa.

The reason a smoke point exists is at first not clear. Initially one would expect the larger the flame the longer the pyrolysis time and thus the greater the tendency to soot. However when the fuel jet size is constant, the larger volumetric flow rate (and thus flame height) is obtained by increasing the fuel velocity. Thus the stay time of a fuel element within the flame is constant, no matter what the height. Then the question arises as to why sufficient soot forms at certain height to break through the flame. We have concluded that as the fuel flow rate is increased, more and more air (though very small quantities) is entrained from the surrounding stream near the fuel port tip into the fuel side of the flame. It is well known that small amounts of oxygen will catalyze the pyrolysis of hydrocarbon fuels. Indeed we had observed this fact in our earlier experiments with additives when we doped our fuel with small amounts of oxygen. We could reduce our smoke points appreciably with the addition of small amounts of oxygen; indeed the smoke point varied with the amount of oxygen added.

There are important consequences of this concept. If indeed it is the induced oxygen which eventually causes a smoke point, then our earlier hypothesis⁴ that the pyrolysis rate of the fuel at a fixed temperature is the controlling factor in sooting tendency is correct.

Experiments were then performed on numerous fuels. For each fuel, we determined the smoke point as a function of the amount of inert diluent added. Two diluents were used - nitrogen and argon. Most of the results were obtained with nitrogen. The results were initially plotted as the volumetric or mass flow rate versus the calculated adiabatic stoichiometric flame temperature for the fuel with the corresponding amount of diluent added. Although for diffusion flames the volumetric flow rate is the more fundamental one, the mass flow rate normalizes the data for comparing fuel types. The plot of flow rate versus temperature gave a series of curves for each fuel that showed most interesting trends. There seemed,

however, to be a more meaningful manner to plot the data.

If the fuel pyrolysis rate were the controlling element in the sooting tendency, then the flow rate at the smoke point (or the sooting height) was an inverse measure of the pyrolysis. And, if the pyrolysis rate followed Arrhenius kinetics, then a plot of the (log of the inverse of the fuel rate) versus $1/T$ should give straight lines. All the data correlated in this manner! Since this work has been published,^{7,8} we only show the most important graph in this report (see Figure 6). In this figure, it is important to compare the results for various fuels at the same temperature. Thus one observes that acetylene is not one of the most prolific sooters. Its tendency to soot only appears great because its ordinary flame temperature is so high.

We observe that the C_4 and C_5 olefins and diolefins have the greater tendency to soot. The results obtained for toluene fall above the olefins and indicate a greater tendency to soot. This observation provides some insight into the chemical mechanism of soot formation and is consistent with some of our early proposals.⁴

The practical importance of these results is that they stress the great importance of the stoichiometric flame temperature in sooting in diffusion flames. Recall there are two temperatures in diffusion flame combustion system: the stoichiometric temperature of the actual flame and the final (lower) temperature which corresponds to the overall stoichiometry determined from the fuel and air flow rates. We shall address this important point again later.

Numerous other experiments were performed to evaluate the effect of oxygen concentration on sooting diffusion flames. The results are shown in Figure 7, in which the sooting height is plotted as a function of the oxygen index (oxygen mole fraction in oxidizer stream). The fact that the tendency to soot undergoes a minimum (maximum sooting height) is indicative of two competing processes in

the test procedure. As the oxygen concentration rises, so does the flame temperature, pyrolysis and the amount of soot formed. But the rate of soot of burn-up also increases. The two processes would have two different activation energies: high for pyrolysis process and low for the burn-up process. At low oxygen concentration as the oxygen index is raised, the rate of burn-up dominates and thus the flame height for sooting must increase. As the concentration is increased further, the flame temperature becomes sufficiently large that the high activation energy process dominates. At this point the rate of fuel pyrolysis, which increases with temperature, dominates and the sooting tendency increases as the oxygen index increases. This model suggests that a more appropriate manner to plot these data would have been sooting height versus the calculated adiabatic flame temperature corresponding to the experimental oxygen index. Different curves of height versus index were obtained when nitrogen and argon were used as the inert in the oxidizer stream. However when the data were plotted as a function of the temperature the nitrogen and argon results fell on the same curve. The details are given in another recently published manuscript.⁹

These results with respect to oxygen index may appear to be in conflict with other results in the literature. Others found and reported that the sooting tendency always decreased with increasing oxygen index. The anomaly is due to the sooting criterion used. We used the sooting height when the soot broke through the luminous zone, whereas others used the presence of soot at the end of the containing cylinder in which the time for particle burn-up was extremely long. When we used the same criterion, we found the same trends as others. However, our results gave the important practical result to limit the amount of soot, one must reduce the flame temperature and one means for doing this is to reduce the oxygen mole fraction by vitiation. Again, the published paper has more extensive

details.

During the subject contract year we also constructed our pre-mixed flame experimental apparatus, but sufficient data had not been obtained to report any results of significance.

IV. SENSITIVITY ANALYSIS STUDIES OF COMBUSTION SYSTEMS*

Combustion phenomena inherently involve a complex interaction of many simultaneous chemical reactions and associated transport phenomena. A central question in this area concerns which features of a chemical mechanism or transport coefficients are responsible for observable events in the laboratory or on an engineering scale. This general question has been very difficult to address due to the complex interaction between the system chemical and transport components. In recognition of this problem, we have been developing a powerful family of sensitivity analysis tools to quantitatively address these questions.^{10,11} These tools are most useful in conjunction with on-line experiments or for the purpose of designing such experiments, and the theory has been tailored with this goal in mind.

In its most elementary form sensitivity analysis concerns an examination of the system gradients. $\frac{\partial c_i(x,t)}{\partial \alpha_j}$ where $c_i(x,t)$ is the i -th species concentration at position x and time t and α_j is the j -th system parameter (e.g., a rate constant or transport coefficient). Other bulk thermodynamic observables could also be considered. An examination of these gradients gives an immediate measure of the relationship between the output observables and the input system parameters. More generally, an entire family of gradients can be generated to address a host of physical questions. The mathematical structure of this theory is very similar to thermodynamics and the table below gives a summary of the general types of ques-

* Contributed by Prof. H. Rabitz, Dept. of Chemistry, Princeton University.

tions that can be addressed.

Applications of Sensitivity Analysis

1. Elementary Sensitivities $\frac{\partial c_i(x,t)}{\partial \alpha_j}$
2. Parameter-Observation Interdependence $\frac{\partial \alpha_j(x,t)}{\partial c_i}$. These gradients are generally not the inverse of those in item 1 since different dependent and independent variables may be involved.
3. Parameter Interdependence $\frac{\partial \alpha_i}{\partial \alpha_j}$. A parameter interdependence develops when certain observations are assumed to be performed.
4. Interdependence of Different Observations $\frac{\partial c_i(x,t;x;t')}{\partial c_j}$.
5. Functional Sensitivity Analysis $\frac{\delta c_i(x,t,x',t)}{\delta \alpha_j}$, $\frac{\delta \alpha_i(x,t,x',t')}{\delta \alpha_j}$, etc.
This is the most general case whereby the parameters themselves may be considered functions of the system coordinates. All items in the table may be extended to the case of functional derivatives.
6. Higher Order Sensitivities $\frac{\partial^2 c_i}{\partial \alpha_j \partial \alpha_k}$, etc.
7. Memory Effects and Stability Analysis $\frac{\partial c_i(x,t)}{\partial c_j(x',t')}$. This gradient is a generalized memory function which measures the stability of the i-th observable at time t_i with respect to variations of the j-th observable at prior time t' . This function should be distinguished from questions of observational interdependence addressed in item 4 which assumes certain observations have actually been made.
8. Position and Time as Dependent Variables $\frac{\partial x}{\partial \alpha_j}$ and $\frac{\partial t}{\partial \alpha_j}$. Critical distances or induction times can legitimately be considered functions of the system parameters.
9. Sensitivity of Objective Functions. Often a desired physical observable is

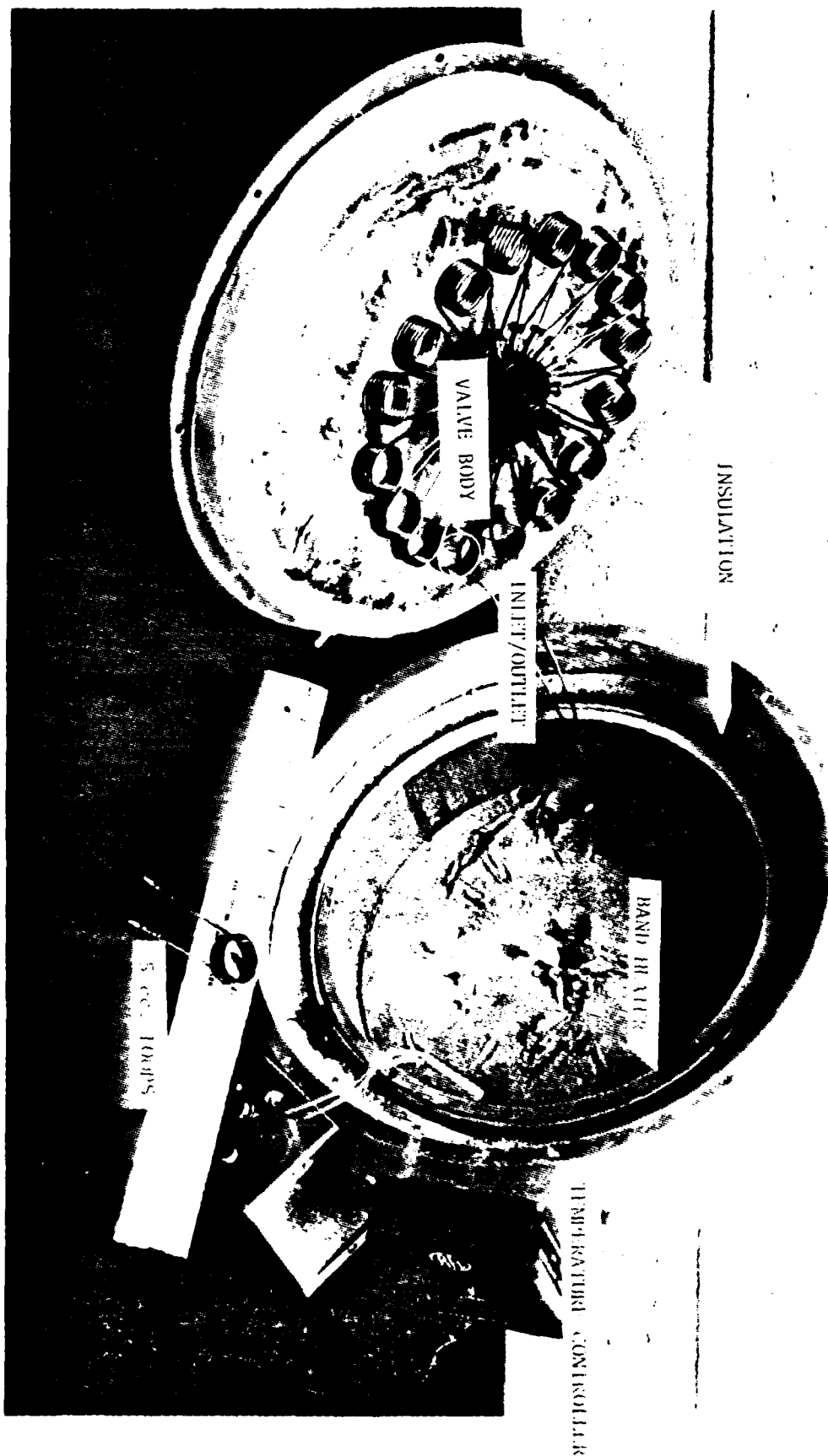
in fact a functional of the output vector \underline{c} . Sensitivities to the desired objective function can readily be generated.

10. Sensitivity to Missing Model Components. The sensitivity of parameters left out of the model may readily be calculated when evaluating the gradients at the nominal null value of the parameters.
11. Structural Sensitivity Analysis. Sensitivity of global features or structures in the observables (e.g. frequencies of oscillating reactions, positions or widths of chemical concentration maxima, etc.) can be readily calculated.
12. Mapping Out Parameter Space. The sensitivity gradients can be used to generate non-linear interpolation formulas for probing the behavior of the multi-dimensional parameter space governing a class of chemical/physical problems.
13. Statistical Error Analysis.

The above table represents the current state of the art in sensitivity theory and continuing research is underway to both extend the usefulness of sensitivity theory as well as carry out practical calculations for combustion oriented problems. In the latter case, one particular area of focus concerns a probing of the interrelationship between transport phenomena and chemical mechanisms which is addressed by item 3 in the table. In order to bring these tools to a wider audience, we are also in the process of developing¹² a streamlined sensitivity code which would be compatible with a variety of existing modelling packages. This work should allow for the addressing of a rich variety of chemical/physical combustion problems which were heretofore impossible to deal with.

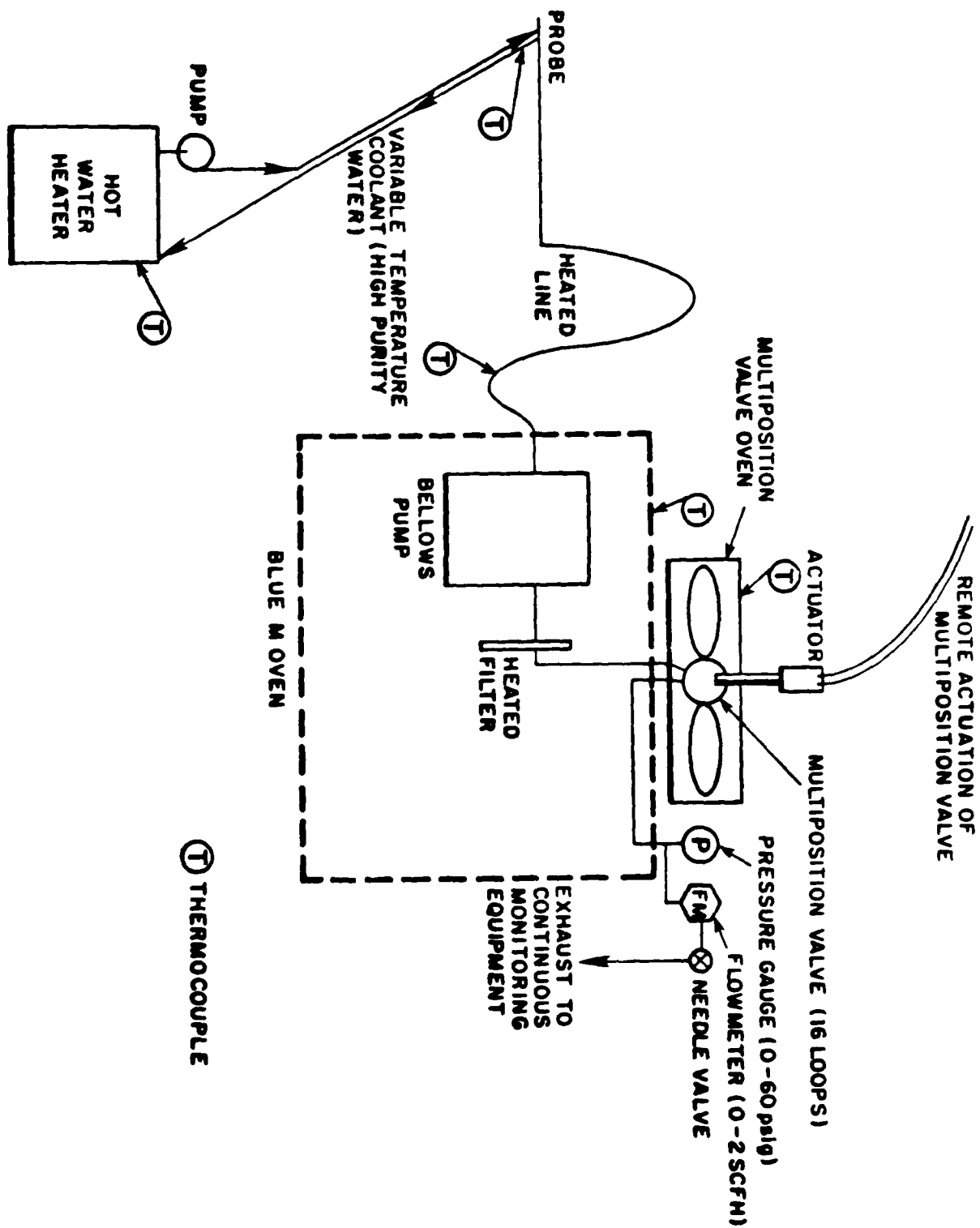
REFERENCES

1. Hautman, D.J., Santoro, R., Dryer, F.L. and Glassman, I., "An Overall and Detailed Kinetic Study of the Pyrolysis of Propane", *Int'l J. of Chemical Kinetics* 13, 149 (1981).
2. Dryer, F.L., "High Temperature Oxidation of Carbon Monoxide and Methane in a Turbulent Flow Reactor", AFOSR Report TR-72-1109, 1972.
3. Euchner, J., "A Study of the Oxidation of Toluene in a Flow Reactor", Princeton University, Department of Mechanical and Aerospace Engineering, M.S.E. Thesis, 1980.
4. Glassman, I., "Phenomenological Models of Soot Processes in Combustion Systems", AFOSR Report TR-79-1147, 1979.
5. Milliken, R.C., "Non-Equilibrium Soot Formation in Pre-Mixed Flames", *J. Phys. Chem.* 66, 784 (1962).
6. Euchner, J.A., Venkat, C., Brezinsky, K. and Glassman, I., "Preliminary Studies on the Oxidation of Aromatics at High Temperatures", accepted for publication in "Proceedings of First International Specialists Meeting of the Combustion Institute".
7. Yaccarino, P.A., "Parametric Study of Sooting Diffusion Flames", Princeton University Report of Mechanical and Aerospace Engineering, M.S.E. Thesis, 1980.
8. Glassman, I. and Yaccarino, P., "The Temperature Effect in Sooting Diffusion Flames", accepted for publication in 18th Symp. (Int'l) on Combustion.
9. Glassman, I. and Yaccarino, P., "The Effect of Oxygen Concentration on Sooting Diffusion Flames", *Comb. Sci. and Tech.* 24, 107 (1980).
10. E. Dougherty and H. Rabitz, "Computational Kinetics and Sensitivity Analysis of Hydrogen-Oxygen Combustion", *J. Chem. Phys.* 72, 6571 (1980).
11. M. Demiralp and H. Rabitz, "Chemical Kinetic Functional Sensitivity Analysis: Elementary Sensitivities", *J. Chem. Phys.*, 1981, in press.
12. M. Kramer, J. Calo and H. Rabitz, "An Improved Computational Method for Sensitivity Analysis - The Green's Function Method with "Aim", manuscript in preparation.



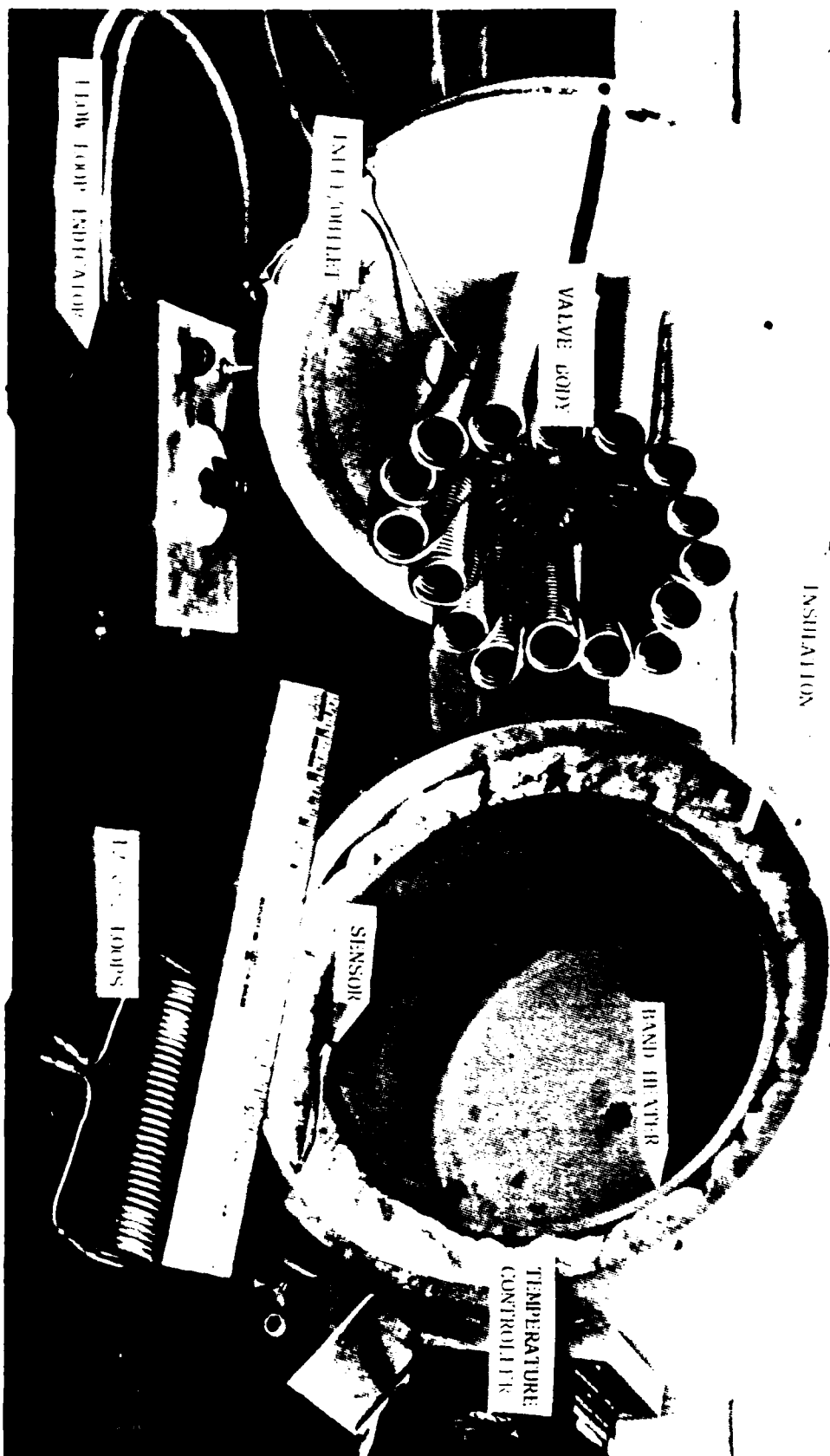
MULTIPOSITION VALVE AND OVEN

FIGURE 1



SAMPLE ACQUISITION SYSTEM SCHEMATIC

FIGURE 2



MULTIPOSITION VALVE AND OVEN

FIGURE 3

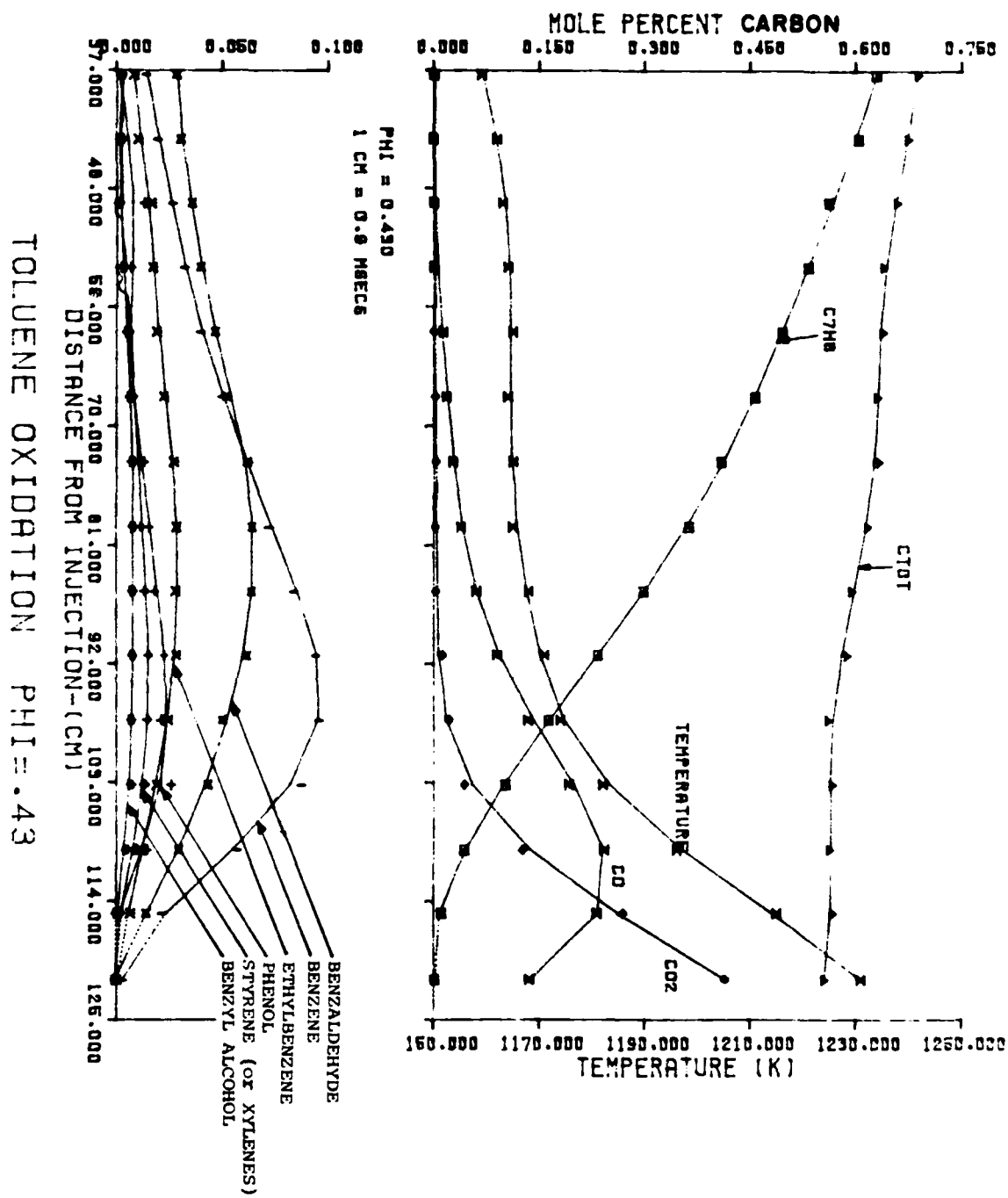


FIGURE 4

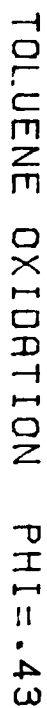
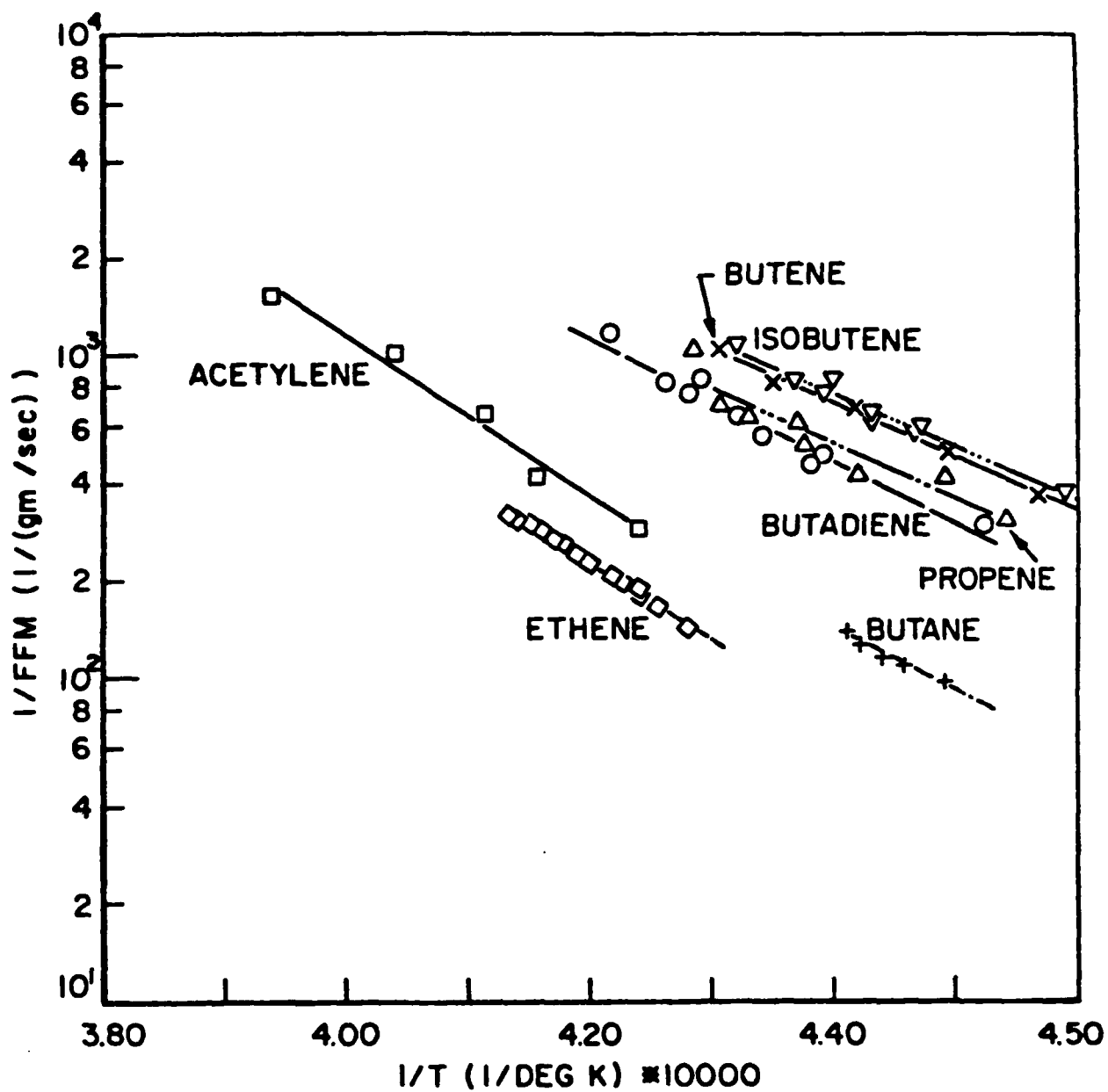


FIGURE 5

FIGURE 6



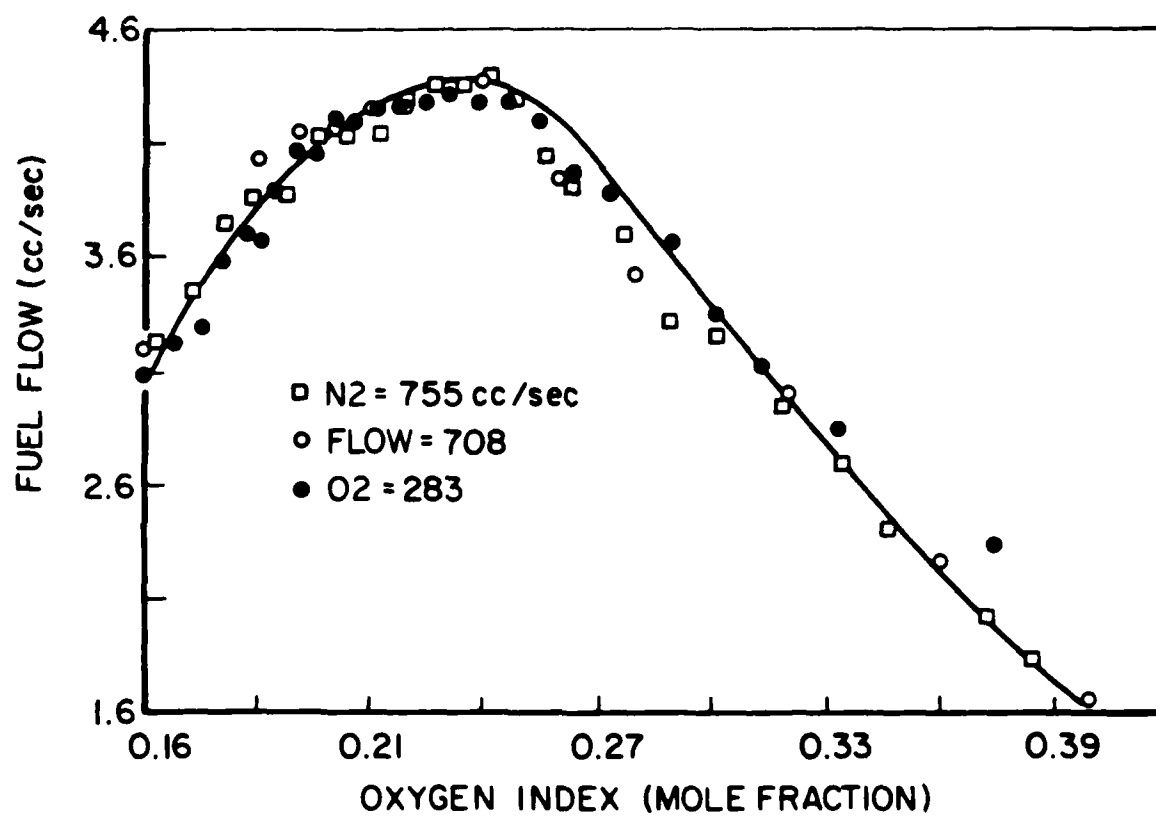


FIGURE 7

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A high temperature sampling system for the Princeton flow reactor has been developed. Initial results have been obtained on the oxidation of toluene Benzaldehyde forms as an important intermediate and then the process becomes one of the oxidizing formly and phenyl reactions. The effects of oxygen index and temperature on sooting diffusion flames have been studied. Results indicate that the stoichiometric flame temperature dominates the sooting tendency and that the C4 and C5 olefine and diolefins and the aromatics are the most dominant sooting fuels. In development, as well are a powerful family of			

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sensitivity analysis tools to quantitatively address the complex interaction between a combustion system's chemical and transport component.

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